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| 13. ABSTRACT (Maximum 200 words)<br><br>Research funded by this grant focused on three areas: First, we have explored the surface chemistry associated with reactions of O <sub>2</sub> , D <sub>2</sub> O, B <sub>2</sub> O <sub>2</sub> and B <sub>2</sub> O <sub>3</sub> with boron thin films grown on Ta(110) through the thermal decomposition of diborane. These reactions were studied mainly with the techniques of X-ray photoelectron spectroscopy and mass analyzed thermal desorption. We find that both O <sub>2</sub> and D <sub>2</sub> O form a B <sub>2</sub> O <sub>3</sub> -like oxide on the surface but that the oxide desorbs mainly as B <sub>2</sub> O <sub>2</sub> . Second, we have studied the reaction of B <sub>2</sub> O <sub>3</sub> and O <sub>2</sub> with graphitic carbon deposited on the Pt(111) surface. Although B <sub>2</sub> O <sub>3</sub> is known to inhibit the oxidation of carbon/carbon composites, we found that B <sub>2</sub> O <sub>3</sub> deposited on a carbon layer on Pt(111) completely removes the surface carbon by oxidizing it at 1000 K to CO(g). Although we also observe the desorption of B <sub>2</sub> O <sub>2</sub> (g) from the surface, we determined that the B <sub>2</sub> O <sub>3</sub> is reduced in the process to elemental boron. Third, we finished some experiments during the first few months of the grant on the oxidation of the LaB <sub>6</sub> (100) surface. |  |   |                                    |  |
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## Summary of Project Goals

The general goal of the project was to obtain a better understanding of the surface chemistry associated with the oxidation of boron and carbon surfaces. Both elements are exceptionally stable, covalently-bonded solids with highly unique crystal structures. The specific reactions under study are loosely related to the problems of oxidation and oxidation inhibition of carbon/carbon composites. The oxidation of boron is relevant to carbon/carbon composites because boron and metal borides are often added to the composites as oxidation inhibitors. It is assumed that boron and metal borides are oxidized to  $B_2O_3$ , which has been found empirically to inhibit the oxidation of carbon/carbon composites. It has been postulated that this is due to the blocking of reactive sites on the carbon surfaces by the  $B_2O_3$ . Our boron oxidation work also provides some continuity with work funded under a previous AFOSR grant. The experimental techniques used included X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and scanning tunneling microscopy (STM).

## Results

### A. Oxidation of Boron

For the boron surfaces we used thin films of boron grown on the Ta(110) surface through the thermal decomposition of  $B_2H_6(g)$  at 650-700 K. The use of thin films of boron on a tantalum single crystal substrate offers several practical experimental advantages compared to the  $\beta$ -rhombohedral boron (111) single crystals that we used in the past. We studied the surface interactions of the boron with both  $O_2$  and  $D_2O$ . The surface oxygen coverage on the boron surfaces, as measured with XPS from the area of the O(1s) peak at a binding energy of 532-534 eV, was monitored as a function of  $O_2$  and  $D_2O$  exposure and surface temperature. The oxygen uptake is low at room temperature but increases with increasing temperature and reaches a maximum at 1000-1100 K for  $O_2$  exposures and at a temperature greater than 800 K for  $D_2O$  exposures. TPD measurements showed that the surface oxide desorbs as  $B_2O_2$  at 1100-1250 K. XPS showed that the surface oxide gives rise to a B(1s) peak at a binding energy of 193.5 eV. This was compared to XPS results for  $B_2O_3$  and  $B_2O_2$  directly deposited on the boron film that have B(1s) binding energies of 193.5 and 192.6 eV respectively. This comparison clearly showed that the reaction with  $O_2$  or  $D_2O$  produced surface  $B_2O_3$ . As the surface temperature was increased, this  $B_2O_3$  reacted with substrate boron to produce  $B_2O_2(g)$ .

To further characterize the properties of  $B_2O_3$  and  $B_2O_2$  while on the boron surface, we carried-out experiments with  $B_2O_2$  and isotopically pure  $^{10}B_2O_3$  directly deposited on the boron film from a Knudsen cell. XPS spectra showed that  $B_2O_2$  disproportionates

to  $B_2O_3$  and boron at temperatures of 600-800 K. TPD experiments show that surface oxide desorption takes place at temperatures of 1100-1250 K and that the dominant desorbing species is  $B_2O_2(g)$  regardless of whether  $B_2O_3$  or  $B_2O_2$  is initially deposited. When isotopically pure  $^{10}B_2O_3$  reacts with the boron film containing the natural abundance  $^{11}B:^{10}B$  ratio of 4:1, the desorbing  $B_2O_2$  also displays a  $^{11}B:^{10}B$  ratio of nearly 4:1. This indicates almost complete exchange of boron atoms between the oxide layer and the boron substrate.

Three publications [6,7,8] resulted from this work. Publication no. 7 focuses on the properties of the boron thin films as determined by XPS and LEED and the interactions of these boron films with  $O_2$  and  $D_2O$ . Publication no. 8 describes results on the reactions of  $B_2O_3$  and  $B_2O_2$  with the boron. Publication no. 6 concerns the detailed XPS characterization of thin films of  $B_2O_2$  deposited on a Ag foil. This latter publication is the first such study of this boron suboxide. It was important to establish the characteristics of this material as our work has shown that it plays an important role in boron oxidation. From this work we have gained a good understanding of the surface chemistry associated with boron oxidation.

#### B. Oxidation of $LaB_6(100)$ .

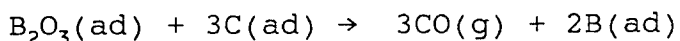
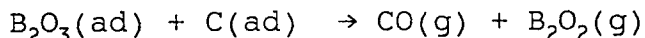
We chose to study the oxidation of  $LaB_6$  for the following reasons: 1) In terms of structure, bonding, and physical properties, elemental boron is closely related to a class of materials known as the boron-rich solids. These materials include metal borides of general formula  $MB_n$  where  $n = 2, 4, 6$ , and 12, and compounds such as boron carbide,  $B_4C$ . Because of the close relationship in other properties between the boron-rich solids and pure boron, we felt it was important to establish if there were any common aspects to the surface chemistry of these materials; 2) As noted above, borides are often added to carbon/carbon composites as oxidation inhibitors with the assumption that these materials will oxidize to  $B_2O_3$ , which is the active agent for the inhibition; 3) Lanthanum hexaboride is a technologically important material as it is the best known thermionic emitter and is therefore widely employed as a cathode in electron guns; 4) Unlike pure boron,  $LaB_6$  has a relatively simple crystal structure and large mounted single-crystals are available.

For the  $LaB_6(100)$  surface we found a high reactivity toward  $O_2$  at both 300 K and at 1000 K as has been observed by others in previous studies. The oxide desorbs as  $LaO(g)$ ,  $BO(g)$  and  $B_2O_2(g)$  at temperatures between 1200 and 1500 K. Although the  $LaO$  and  $BO$  desorption shows little dependence on initial oxidation temperature, the amount of  $B_2O_2(g)$  that desorbs is significantly higher following a 1000 K oxygen exposure. The desorption behavior of all three observed oxides depends on the details of how the clean surface is prepared. This aspect of the oxidation can be related to our previous results on the structure of the

clean surface as revealed through atomically-resolved images we obtained with scanning tunneling microscopy [7,8]. These oxidation results are described in detail in John Ozcomert's PhD dissertation and in references 9 and 10.

### C. The reaction of B<sub>2</sub>O<sub>3</sub> with Carbon

Although we had originally proposed to use HOPG graphite as a model carbon surface, we instead chose to study graphitic islands of carbon grown on the Pt(111) surface through the thermal decomposition of C<sub>2</sub>H<sub>4</sub>(g). Studies by other groups have shown that scanning tunneling microscopy (STM) can be used to give atomically resolved images of the graphitic islands and that other forms of carbon can be produced on the Pt(111) surface by varying the deposition conditions. There are several important practical experimental advantages to this approach. In addition, it has the key advantage of providing a much higher proportion of edge to basal plane sites than does HOPG graphite. Although our main goal was to understand how B<sub>2</sub>O<sub>3</sub> inhibits the oxidation of carbon, we discovered that at sufficiently high temperatures B<sub>2</sub>O<sub>3</sub> is a highly effective oxidant of graphite; it completely removes carbon from the surface in the form of CO(g) at temperatures of 1000-1100 K. This observation is consistent with each of the following reactions:



Although we observed some B<sub>2</sub>O<sub>2</sub>(g) desorption, a detailed analysis showed that the second reaction describes the reduction of B<sub>2</sub>O<sub>3</sub>(ad). The B<sub>2</sub>O<sub>2</sub>(g) that we observed is attributed to the reduction of B<sub>2</sub>O<sub>3</sub>(ad) by the boron produced in the first reaction. This work has been published (ref 11).

Our original plans called for investigating the influence of B<sub>2</sub>O<sub>3</sub> on the oxidation of carbon with STM. Our strategy was to study the reaction using graphitic monolayers on the Pt(111) surface. As part of this goal we reproduced earlier thermal desorption work on the reaction of oxygen with graphitic monolayers. We also reproduced STM images of graphitic islands on the Pt(111) surface. We were about to begin the STM studies of the oxidation reaction with and without coadsorbed B<sub>2</sub>O<sub>3</sub> when we were informed that the decision to fund option 2 of the grant was being reversed. This forced us to scale back our plans. As a result little progress was made in the no-cost extension period of March 15-September 15, 1994.

### D. Future Directions

We received AFOSR funding for our work on the surface structure and chemistry of boron and related materials from January 1988 through September 1994. We do not expect to receive

or to seek AFOSR funding for our work for the foreseeable future. During the period that we were funded by AFOSR we established a unique laboratory and expertise in the surface chemistry of the boron-rich solids. I have been actively seeking, with some success, new sources of funding for this work. In addition, we have established contacts with high-technology companies with a direct interest in these materials. In short, the sudden termination of AFOSR funding for our work has not led us to abandon this area of research. My laboratory at the University of Illinois at Chicago will continue to be a center of excellence for research on the surface science of the boron-rich solids.

### Publications

#### Based on Previous Grant (AFOSR 88-0111)

1. Wei Cho Foo, John S. Ozcomert, and Michael Trenary, "The Oxidation of the  $\beta$ -Rhombohedral Boron (111) Surface", *Surf. Sci.* 255, 245 (1991)
2. Wei Cho Foo, John S. Ozcomert and Michael Trenary, "The Reactions of  $B_2O_3$  and  $O_2$  with the  $\beta$ -Rhombohedral Boron (111) Surface", in Boron-Rich Solids, (AIP Conference Proceedings 231), D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, C. L. Beckel, eds., (American Institute of Physics, New York 1991) p. 643
3. Wei Cho Foo, John S. Ozcomert, and Michael Trenary, "The Reaction of  $B_2O_3$  with the  $\beta$ -Rhombohedral Boron (111) Surface", *Surf. Sci.* 262, 88 (1992)
4. John S. Ozcomert and Michael Trenary, "Atomically Resolved Surface Structure of  $LaB_6(100)$ ", *Surf. Sci.* 265 L227 (1992)
5. John S. Ozcomert and Michael Trenary, "The Atomically Resolved Surface Structure of  $LaB_6(100)$  as Observed with Scanning Tunneling Microscopy", *J. Vac. Sci. Technol. A* 10, 2581 (1992)

#### Based on Current Grant (F49620-92-0179)

6. Y. Wang and Michael Trenary, "Characterization with XPS of a Thin Film of  $B_2O_2$  Deposited on a Ag Substrate", *Surface Science Spectra*, 1, 183 (1992)
7. Y. Wang and Michael Trenary, "The Surface Chemistry of Boron Oxidation. I The Reaction of  $O_2$  with a Boron Film Grown on Ta(110)", *Chemistry of Materials*, 5, 192 (1993)
8. Y. Wang and Michael Trenary, "The Surface Chemistry of Boron Oxidation. II The Reaction of  $B_2O_3$  and  $B_2O_2$  with a Boron Film Grown on Ta(110)", *Chemistry of Materials*, 5, 199 (1993)

9. J. S. Ozcomert and Michael Trenary, "Oxide Thermal Desorption from the  $\text{LaB}_6(100)$  Surface following Reaction with  $\text{O}_2$ ", Chemistry of Materials, 5, 1762 (1993)
10. J. S. Ozcomert and M. Trenary, "High Temperature Evaporation of Oxides from the  $\text{LaB}_6(100)$  Surface Following Reaction with Water", Proc. 11th In. Symp. Boron, Borides and Related Compounds, Tsukuba, 1993, JJAP Series 10 (1994) pp. 174-177
11. J. Vetrone, J. Fan, M. Trenary, "Oxidation of Graphite Monolayers on  $\text{Pt}(111)$  by  $\text{B}_2\text{O}_3$ ", Surface Science, 314 315, (1994)

#### Personnel

The following personnel were supported on this grant.

Michael Trenary, Professor and PI, received two months summer salary in 1992 and 1993.

John S. Ozcomert, graduate research assistant, US citizen. Received PhD, June 1992, supported from March 15, 1992 to July 1, 1992. Dissertation title: "Structure and Reactivity of the  $\text{LaB}_6(100)$  Surface".

Yajun Wang, graduate research assistant, citizen of China, supported from March 15, 1992 to August 1, 1992. Transferred to another university after receiving Masters Degree.

Yumee Koo, graduate research assistant, citizen of South Korea, supported from January 11, 1993 to December 31, 1993. Was advised to change research groups upon unexpected termination of this grant.

James Vetrone, postdoctoral associate, PhD in Materials Science from Northwestern University, postdoctoral advisor: Yip Wah Chung. One year contact: September, 1992 through August 1993.

Craig Perkins, US citizen, supported during summers of 1992 and 1993 and fall semester 1993.